

5           ELECTROCHEMICAL CELL HAVING A PHYSICAL VAPOR  
DEPOSITED ELECTRODE AND METHOD OF MANUFACTURE

## CROSS-REFERENCE TO RELATED APPLICATION

10           The present application is a divisional of  
application Serial No. 09/498,667, filed February 7,  
2000, which claims priority based on provisional  
application Serial No. 60/118,977, filed February 8,  
1999.

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## BACKGROUND OF THE INVENTION

## 1.   Field Of The Invention

20           The present invention generally relates to the art  
of electrical energy storage devices and more  
particularly, to an electrode of an electrochemical cell  
or capacitor produced by a physical vapor deposition  
process.

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## 2.   Prior Art

30           Physical vapor plating involves introducing a  
material of interest into a vacuum and heating to a  
temperature at which the material reaches its vapor  
pressure. When molecular rays of the vaporized material  
attain a sufficient energy such that their mean free  
path causes them to impinge upon and precipitate onto a  
substrate, a coating of the material is formed. While  
35          physical vapor deposition processes are known in the

5 art, as of yet, they have not been used to deposit an  
electrode active material onto a substrate to provide an  
electrode component for an electrochemical cell and to  
deposit a semiconductive or pseudocapacitive material  
onto a substrate to provide an electrode component for a  
10 capacitor.

#### SUMMARY OF THE INVENTION

The present invention is directed to a novel and  
15 unique application of the physical vapor deposition  
process. The present process provides a coating of an  
electrochemically active material on a substrate,  
preferably a conductive substrate. The thusly produced  
coated substrate is useful as an electrode, for example,  
20 a cathode electrode incorporated into a primary  
electrochemical cell, and as the anode and/or the  
cathode of a secondary electrochemical cell. The  
assembly of the cell incorporating the electrode  
component made by physical vapor depositing an electrode  
25 active material onto a conductive substrate according to  
the present invention is preferably in the form of a  
wound element cell. That is, the fabricated cathode  
together with an anode and a separator are wound  
together in a "jellyroll" end type configuration or a  
30 "wound element cell stack" such that the anode is on the  
outside of the roll to make electrical contact with the  
cell case in a case-negative configuration. Other types  
of cells such as prismatic, bobbin shape and flat cells  
are also possible with the present invention.

5        In the case of a capacitor, the present physical vapor deposition process is useful for producing an anode or a cathode in an electrochemical capacitor or the cathode in an electrolytic capacitor. Regardless 10      the type, the capacitor configuration generally includes a substrate of a conductive metal such as titanium or tantalum provided with a semiconductive or a pseudocapacitive oxide coating, nitride coating, carbon nitride coating, or carbide coating.

15      DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

One embodiment of the present invention is directed to the use of a physically vapor deposited coating of an electrode active material on a conductive substrate to 20      thereby form an electrode component for an electrochemical cell. In one preferred embodiment, the electrode active material is a cathode active material deposited onto a substrate by means of a physical vapor deposition process to form a cathode component for an 25      electrochemical cell. The cathode active material is selected from the group consisting of a metal, a metal oxide, mixed metal oxide, a metal sulfide and a carbonaceous material, and mixtures thereof. Suitable cathode materials include silver vanadium oxide, copper 30      silver vanadium oxide, manganese dioxide, titanium disulfide, copper oxide, cobalt oxide, chromium oxide, copper sulfide, iron sulfide, iron disulfide, carbon and fluorinated carbon. The solid cathode exhibits

5 excellent thermal stability and is generally safer and less reactive than a non-solid cathode.

Preferably, the solid cathode material comprises a mixed metal oxide formed by physical vapor depositing various metal oxides or metal oxide/elemental metal 10 combinations. The materials thereby produced contain metals and oxides of Groups IB, IIB, IIIB, IVB, VB, VIB, VIIB and VIII of the Periodic Table of Elements, which includes the noble metals and/or their oxide compounds.

By way of illustration, and in no way intended to 15 be limiting, an exemplary cathode active material comprises silver vanadium oxide having the general formula  $Ag_xV_2O_y$  in any one of its many phases, i.e.  $\beta$ -phase silver vanadium oxide having in the general formula  $x = 0.35$  and  $y = 5.18$ ,  $\gamma$ -phase silver vanadium 20 oxide having in the general formula  $x = 0.74$  and  $y = 5.37$  and  $\epsilon$ -phase silver vanadium oxide having in the general formula  $x = 1.0$  and  $y = 5.5$ , and combination and mixtures of phases thereof. Preferably, the cathode active material, whether comprised of silver vanadium 25 oxide or a similarly suitable material, is deposited onto a substrate of titanium, stainless steel, nickel, tantalum, platinum, gold or aluminum by a physical vapor deposition process. The thusly formed exemplary electrode can be incorporated into an alkali metal 30 electrochemical cell, and more particularly, a lithium electrochemical cell.

Another preferred embodiment of the present invention comprises coating an alkaliated material onto a conductive substrate of the above described materials by

5 a physical vapor deposition process to provide a cathode  
for a secondary electrochemical cell. For example, in  
the case of the alkaliated material being a lithiated  
material suitable materials include oxides, sulfides,  
selenides and tellurides of such metals as vanadium,  
10 titanium, chromium, copper, tin, molybdenum, niobium,  
iron, nickel, cobalt and manganese. Among the suitable  
oxides are  $\text{LiNiO}_2$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiCoO}_2$ ,  $\text{LiCo}_{0.92}\text{Sn}_{0.08}\text{O}_2$  and  
 $\text{LiCo}_{1-x}\text{Ni}_x\text{O}_2$ . The anode for such a secondary  
electrochemical cell can comprise a particulate  
15 carbonaceous composition including carbon together with  
a filamentary, electrically conductive material such as  
carbon black. Accordingly, it is further contemplated  
by the scope of the present invention that particulate  
carbonaceous compositions are physically vapor deposited  
20 onto a conductive substrate for use as an anode  
component in a secondary cell and as the cathode in a  
primary electrochemical cell.

Physical vapor deposited coatings rely mostly upon  
mechanical bonding to the substrate surface. It is,  
25 therefore, critical that the electrode substrate be  
properly prepared to ensure coating quality. It is  
especially necessary that the surface remain  
uncontaminated by lubricants from handling equipment or  
body oils from the hands. Suitable substrate surface  
30 preparation techniques include scraping, wire brushing,  
machining, grit blasting, or by chemical action. It  
also is recommended that the prepared surface be coated  
as soon as possible after preparation to prevent the  
possibility of contamination or surface oxidation.

5        After substrate surface cleaning, surface roughness  
is the next most critical factor for properly applying a  
physical vapor deposited coating of electrode active  
material. Three methods of roughening the electrode  
substrate surface are appropriate and they consist of  
10      rough threading, grit blasting, and a combination of  
rough threading, then grit blasting, as are well known  
to those skilled in the art of chemical vapor deposition  
techniques.

15      According to the present invention any one of the  
previously listed electrode active materials including  
the enumerated cathode active materials and the  
lithiated materials is heated in a vacuum to a  
temperature at which the material reaches its vapor  
pressure. A suitable vacuum pressure is about  $10^{-2}$  torr  
20      (about  $10^{-5}$  atm) or greater. Under such processing  
conditions, the vaporized material emits molecular rays  
in all directions. The vacuum must be great enough that  
the mean free path of the residual gas molecules is  
greater than the distance from the material evaporation  
25      source to the substrate being coated. Accordingly, the  
physical vapor deposition process of the present  
invention requires that the molecular vapor travel from  
its source to the substrate to form the desired coating  
without intermediate collision and precipitation.

30      One of the benefits of the present invention is  
that electrode plates made by a physical vapor  
deposition process according to the present invention  
are thinner than currently available electrodes. This  
provides for the manufacture of higher surface area

5 cells housed in smaller containers than conventional electrode preparation technology permits. In that respect, the electrode active material can be coated on both sides of the substrate by a physical vapor deposition process to further increase the electrode 10 active surface area. The substrate can also be perforated so that the coatings on both sides of the substrate are in physical contact with each other to lock the electrode active material onto the substrate.

15 The exemplary cell of the present invention having the cathode component made by the physical vapor deposition of a cathode active material onto a suitable substrate and preferably silver vanadium oxide deposited onto a titanium substrate, further comprises an anode selected from Group IA of the Periodic Table of 20 Elements, including lithium, sodium, potassium, etc., and their alloys and intermetallic compounds including, for example Li-Si, Li-B and Li-Si-B alloys and intermetallic compounds. The preferred anode comprises lithium.

25 The form of the anode may vary, but preferably the anode is a thin metal sheet or foil of the anode metal, pressed or rolled on a metallic anode current collector, i.e., preferably comprising nickel to form an anode component. In the electrochemical cell of the present 30 invention, the anode component has an extended tab or lead of the same material as the anode current collector, i.e., preferably nickel integrally formed therewith such as by welding and contacted by a weld to a cell case of conductive metal in a case-negative

5     electrical configuration. Alternatively, the anode may  
be formed in some other geometry, such as a bobbin  
shape, cylinder or pellet to allow an alternate low  
surface area cell design.

The exemplary cell of the present invention having  
10    the cathode component made by physical vapor depositing  
a cathode active material onto a suitable substrate  
includes a separator to provide physical separation  
between the anode and cathode active electrodes. The  
separator is of electrically insulative material to  
15    prevent an internal electrical short circuit between the  
electrodes, and the separator material also is  
chemically unreactive with the anode and cathode active  
materials and both chemically unreactive with and  
insoluble in the electrolyte. In addition, the  
20    separator material has a degree of porosity sufficient  
to allow flow therethrough of the electrolyte during the  
electrochemical reaction of the cell. Illustrative  
separator materials include non-woven glass,  
polypropylene, polyethylene, glass fiber material,  
25    ceramics, a polytetrafluorethylene membrane commercially  
available under the designations ZITEX (Chemplast Inc.),  
a polypropylene membrane commercially available under  
the designation CELGARD (Celanese Plastic Company Inc.)  
and DEXIGLAS (C.H. Dexter, Div., Dexter Corp.). Other  
30    separator materials that are useful with the present  
invention include woven fabric separators comprising  
halogenated polymeric fibers, for example of the type  
described in U.S. Patent No. 5,415,959 to Pyszczek et  
al., which is assigned to the assignee of the present

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5 invention and incorporated herein by reference. Other suitable halogenated polymeric materials include, but are not limited to, polyethylene tetrafluoroethylene which is commercially available under the name Tefzel, a trademark of the DuPont Company;

10 polyethylenechlorotrifluoroethylene which is commercially available under the name Halar, a trademark of the Allied Chemical Company and polyvinylidene fluoride.

15 The form of the separator typically is a sheet which is placed between the anode and cathode electrodes and in a manner preventing physical contact therebetween. Such is the case when the anode is folded in a serpentine-like structure with a plurality of cathode plates disposed intermediate the anode folds and 20 received in a cell casing or when the electrode combination is rolled or otherwise formed into a cylindrical "jellyroll" configuration.

25 The exemplary electrochemical cell of the present invention having the cathode component made by physical vapor depositing a cathode active material onto a suitable substrate further includes a nonaqueous, ionically conductive electrolyte activating the anode and the cathode electrodes. The electrolyte serves as a medium for migration of ions between the anode and the 30 cathode during the electrochemical reactions of the cell. The electrochemical reactions at the electrodes involves conversion of the migrating ions into atomic or molecular forms. Thus, nonaqueous electrolytes suitable for the present invention are substantially inert to the

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5 anode and cathode materials, and they exhibit those physical properties necessary for ionic transport, namely, low viscosity, low surface tension and wettability.

A suitable electrolyte has an inorganic, ionically 10 conductive salt dissolved in a nonaqueous solvent, and more preferably, the electrolyte includes an ionizable alkali metal salt dissolved in a mixture of aprotic organic solvents comprising a low viscosity solvent and a high permittivity solvent. The ionically conductive 15 salt serves as the vehicle for migration of the anode ions to intercalate or react with the cathode active material. In a solid cathode/electrolyte system, the preferred ion-forming alkali metal salt is similar to the alkali metal comprising the anode. Examples of 20 salts useful with the present invention include LiPF<sub>6</sub>, LiAsF<sub>6</sub>, LiSbF<sub>6</sub>, LiBF<sub>4</sub>, LiAlCl<sub>4</sub>, LiNO<sub>3</sub>, LiGaCl<sub>4</sub>, LiSO<sub>3</sub>F, LiB(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>, LiClO<sub>4</sub>, LiC(SO<sub>2</sub>CF<sub>3</sub>)<sub>3</sub>, LiSCN, LiO<sub>3</sub>SCF<sub>2</sub>CF<sub>3</sub>, LiO<sub>2</sub>, LiC<sub>6</sub>F<sub>5</sub>SO<sub>3</sub>, LiO<sub>2</sub>CCF<sub>3</sub>, LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> and LiCF<sub>3</sub>SO<sub>3</sub>, and mixtures thereof.

25 Low viscosity solvents include tetrahydrofuran (THF), methyl acetate (MA), diglyme, triglyme, tetraglyme, dimethyl carbonate (DMC), 1,2-dimethoxyethane (DME), diethyl carbonate, diisopropylether, 1,2-diethoxyethane (DEE), 1-ethoxy,2- 30 methoxyethane (EME), dipropyl carbonate (DPC), ethylmethyl carbonate (EMC), methylpropyl carbonate (MPC) and ethylpropyl carbonate (EPC), and mixtures thereof, and high permittivity solvents include cyclic carbonates, cyclic esters and cyclic amides such as

5 propylene carbonate (PC), butylene carbonate (BC),  
ethylene carbonate (EC), acetonitrile, dimethyl  
sulfoxide, dimethyl formamide, dimethyl acetamide,  
 $\gamma$ -valerolactone,  $\gamma$ -butyrolactone (GBL) and N-methyl-  
pyrrolidinone (NMP) and mixtures thereof. In the  
10 preferred electrochemical cell comprising the Li/SVO or  
the Li/CSVO couple, the preferred electrolyte is 1.0M to  
1.4M LiPF<sub>6</sub> or LiAsF<sub>6</sub> in a 50:50 mixture, by volume, of PC  
and DME.

One preferred form of the cell assembly described  
15 herein is referred to as a wound element cell. That is,  
the fabricated cathode, anode and separator are wound  
together in a "jellyroll" end type configuration or  
"wound element cell stack" such that the anode is on the  
outside of the roll to make electrical contact with the  
20 cell case in a case negative configuration. Using  
suitable top and bottom insulators, the wound cell stack  
is inserted into a metallic case of a suitable size  
dimension. The metallic case may comprise materials  
such as stainless steel, mild steel, nickel-plated mild  
25 steel, titanium or aluminum, but not limited thereto, so  
long as the metallic material is compatible for use with  
components of the cell.

The cell header comprises a metallic disc-shaped  
body with a first hole to accommodate a glass-to-metal  
30 seal/terminal pin feedthrough and a hole for electrolyte  
filling. The glass used is of a corrosion resistant  
type having from between about 0% to about 50% by weight  
silicon such as CABAL 12, TA 23 or FUSITE 425 or FUSITE  
435. The positive terminal pin feedthrough preferably

5 comprises titanium although molybdenum and aluminum can also be used. The cell header comprises elements having compatibility with the other components of the electrochemical cell and is resistant to corrosion. The cathode lead is welded to the positive terminal pin in  
10 the glass-to-metal seal and the header is welded to the case containing the electrode stack. The cell is thereafter filled with the electrolyte described hereinabove and hermetically sealed such as by close-welding a stainless steel ball over the fill hole,  
15 but not limited thereto. This above assembly describes a case negative cell which is the preferred construction of the exemplary cell of the present invention. As is well known to those skilled in the art, the exemplary electrochemical system of the present invention can also  
20 be constructed in a case positive configuration.

Another embodiment of the present invention is directed to the use of a physically vapor deposited coating of a semiconductive or pseudocapacitive oxide coating, nitride coating, carbon nitride coating, or  
25 carbide coating. The coating is deposited on a substrate of a conductive metal such as titanium, molybdenum, tantalum, niobium, cobalt, nickel, stainless steel, tungsten, platinum, palladium, gold, silver, copper, chromium, vanadium, aluminum, zirconium,  
30 hafnium, zinc and iron, and mixtures and alloys thereof. The semiconductive or pseudocapacitive material includes an oxide of a first metal, or a precursor thereof, the nitride of the first metal, or a precursor thereof, the carbon nitride of the first metal, or a precursor

5 thereof, and/or the carbide of the first metal, or a precursor thereof, the oxide, nitride, carbon nitride and carbide of the first metal having pseudocapacitive properties. The first metal is preferably selected from the group consisting of ruthenium, cobalt, manganese, 10 molybdenum, tungsten, tantalum, iron, niobium, iridium, titanium, zirconium, hafnium, rhodium, vanadium, osmium, palladium, platinum, and nickel.

The porous coating may also include a second or more metals. The second metal is in the form of an 15 oxide, a nitride, a carbon nitride or a carbide, or precursors thereof and is not essential to the intended use of the coated foil as a capacitor electrode and the like. The second metal is different than the first metal and is selected from one or more of the group 20 consisting of tantalum, titanium, nickel, iridium, platinum, palladium, gold, silver, cobalt, molybdenum, ruthenium, manganese, tungsten, iron, zirconium, hafnium, rhodium, vanadium, osmium, and niobium. In a preferred embodiment of the invention, the porous 25 coating includes oxides or ruthenium and tantalum, or precursors thereof.

The thusly fabricated semiconductive or pseudocapacitive coated substrates are useful as an anode or a cathode in an electrochemical capacitor or 30 the cathode in an electrolytic capacitor. For additional disclosure directed to such capacitors, reference is made to U.S. Patent No. 5,926,362 to Muffoletto et al., which is assigned to the assignee of the present invention and incorporated herein by

5 reference. For a more thorough understanding of the  
chemical vapor deposition process, reference is made to  
the book Vapor Deposition, edited by Carroll F. Powell,  
Joseph H. Oxley and John M. Blocker, Jr. of the Battelle  
Memorial Institute, Columbus, Ohio, published by John  
10 Wiley & Sons, Inc., the disclosure of which is  
incorporated herein by reference.

It is appreciated that various modifications to the  
invention concepts described herein may be apparent to  
those skilled in the art without departing from the  
15 spirit and the scope of the present invention defined by  
the hereinafter appended claims.